OPTICAL LIMITING WINDOWS FOR EYE AND SENSOR PROTECTION FROM LASER RADIATION

Final Technical Report

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13. ABSTRACT *(Maximum 200 words)*

Report developed under STTR contract. The goal of this Phase I program was to demonstrate the feasibility of fabricating optical power limiting windows having laser radiation resistance, mechanical hardness, and optical quality necessary for military and commercial applications. Two synthetic approaches were pursued: 1) mixed organic/glass composites prepared by incorporating the organic dopants in the initial sol-gel mixture, and 2) mixed organic/glass composites prepared by impregnating a porous glass with organic dopants. Power limiting measurements on glasses containing a substitued fullerene indicated excited state cross sections over 70% of the value for the fullerene in a solvent. Power limiting measurements of post-doped glasses containing a silicon(IV) naphthalocyanine indicated excited state cross sections comparable to the performance of the dye in a solvent. Radiation hardness was also measured on both types of materials and found to be approximately one order of magnitude greater than that of the dye in a solvent. Mold development allowed for direct casting of glasses with greatly improved optical surfaces. The promising results from this Phase I program have provided the basis for a proposed Phase II program which would take this technology to a level suitable for commercialization in Phase III.

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EXECUTIVE SUMMARY

The vulnerability of human eyes and sensing devices to high power laser radiation presents a critical need in both the military and private sectors for protection devices. These devices must permit normal eye and sensor functions while blocking all damaging wavelengths when subjected to high power radiation. Optical power limiting provides just such a mechanism for this type of passive protection.

In order for these non-linear optical materials to be useful for optical power limiting applications they must be incorporated into solid-state materials having a high damage threshold. Sol-gel materials are especially promising because of the synthetic versatility of the process by which they are produced, and because their relatively high silica content results in materials with potentially high damage thresholds. Using the sol-gel approach, scientists at Los Alamos have patented techniques for producing composite glasses containing fullerenes or fullerene derivatives having high damage thresholds [10].

The goal of the Phase I STTR program was to demonstrate the feasibility of fabricating optical power limiting windows having laser radiation resistance, mechanical hardness, and optical quality necessary for military and commercial applications. The program brings together two organizations recognized as leaders in their respective fields: Los Alamos National Laboratory, along with their collaboration with Professor Joe Wudl at the University of California Santa Barbara, is a leader in the synthesis and characterization of substituted fullerenes and fullerene-doped sol-gel glasses. GELTECH, Inc. is a leader in the development and commercialization of molded porous and dense silica glasses via the sol-gel process.

Two different synthetic approaches which have shown promise were pursued in this program:

1. Mixed organic/glass composites were prepared by incorporating the organic dopants in the initial sol-gel mixture. These will be termed pre-doped glasses.

2. Mixed organic/glass composites were prepared by first producing a porous glass, treating the surface of the pores with a hydrophobic material, and then impregnating these materials with organic dopants. These will be termed post-doped glasses.

In addition to these two synthetic approaches, mold development was pursued in order to produce doped windows with smooth, flat surfaces with reduced optical scattering losses.

Power limiting measurements were made on both pre-doped and post-doped glasses containing a substitued fullerene (PCBM), and the results were very promising. Excited state cross sections were measured to be over 70% of the value for the fullerene in a solvent.

Power limiting measurements were made on post-doped glasses containing a silicon(IV) naphthalocyanine (SiNc), and the results were even more promising. The power limiting was found to be comparable to the performance of the dye in a solvent.

Radiation hardness was also measured on both types of materials and found to be approximately one order of magnitude greater than that of the dye in a solvent.

Mold development resulted in a strategy which allowed for direct casting of pre-doped glasses with improved optical surfaces. This improvement was noticeable in two ways. First, the distortion due to lensing by non-planar surfaces was reduced to be acceptable with optical quality to be expected of 2 mm thick windows. Second, the level of optical scattering relative to non-molded samples was reduced at least four-fold, so that the net scattering loss in the molded glass samples in the visible spectrum was <5%. Furthermore, the mold design is one which can be adapted to production levels for commercialization purposes.

The promising results from this Phase I program have provided the basis for a proposed Phase II program which would take this technology to a level suitable for commercialization in Phase III.

I. INTRODUCTION

The vulnerability of human eyes and sensing devices to high power laser radiation presents a critical need in both the military and private sectors for protection devices. These devices must permit normal eye and sensor functions while blocking all damaging wavelengths when subjected to high power radiation. Optical power limiting provides just such a mechanism for this type of passive protection.

Optical limiting has been investigated in a number of materials with distinct nonlinear mechanisms [1]. Of these materials, the most widely investigated are:

1. Organic and organometallic molecules which rely on reverse saturable absorption (RSA). The more promising RSA materials include heavy-atom-substituted phthalocyanines [2,3], porphyrins [4], and fullerenes [5]. The phthalocyanines have demonstrated superiority at the most commonly investigated wavelength of 532 nm, and show optical power limiting for a range of wavelengths in the visible spectral region. Very recent studies have shown enhanced properties of fullerenes in the red and near-IR [6,7,8,9].

2. Colloidal carbon suspensions, which rely on nonlinear scattering. While they yield broadband limiting in the near-IR, carbon suspension materials are widely regarded as unsatisfactory, especially in view of the requirement that they be used in a liquid state.

In order for these non-linear optical materials to be useful for optical power limiting applications they must be incorporated into solid-state materials having a high damage threshold.

Two of the more common materials which have been pursued for the inclusion of optically active molecules in a solid matrix are: 1) polymers, such as PMMA, and 2) composite glasses produced by the sol-gel process. The use of PMMA has been demonstrated, but the damage threshold of PMMA is extremely low, thereby limiting its usefulness. Sol-gel materials are especially promising because of the synthetic versatility of the process by which they are produced, and because their relatively high silica content results in materials with potentially high damage thresholds. Using the sol-gel approach, scientists at Los Alamos have patented techniques for producing composite glasses containing fullerenes or fullerene derivatives having high damage thresholds [10].

The goal of the Phase I STTR program was to demonstrate the feasibility fabricating optical power limiting windows having laser radiation mechanical hardness, and optical quality necessary for military and commercial applications.

Successful completion of Phase I has established the foundation for the development necessary to take this technology from its present laboratory stage to a readiness for commercialization by the end of Phase II.

II. PHASE I PROGRAM STRATEGY

To meet the stated objectives of this program, two different synthetic approaches which have shown promise were pursued. An important goal in the development of synthetic methods was to

demonstrate that similar techniques could be applied to a range of organic nonlinear absorber dyes from the most promising classes of materials, including fullerenes, phthalocyanines, and porphyrins.

1. Mixed organic/glass composites were prepared by incorporating the organic dopants in the initial sol-gel mixture. These mixtures will be termed pre-doped gels. This approach has been extensively pursued by Los Alamos and has resulted in one patent being issued and another pending. This formed much of the basis of the Phase I work for producing glasses with lower densification temperatures and improved optical clarity and mechanical properties.

2. Mixed organic/glass composites were prepared by first producing a porous glass and then impregnating these materials with organic dopants. These mixtures will be termed post-doped gels. A primary advantage of this approach is that the porous glass can be heated to high temperatures (~800°C) to maximize its mechanical and optical properties before impregnation. GELTECH has more than 10 years experience in the sol-gel process, and routinely manufactures 25, 50, 75, and 200Å pore diameter porous gels, some in very large commercial quantities. Researchers at GELTECH have patents on the impregnation of organic and inorganic materials in sol-gel matrices, and have publications relating to this work [11,12,13].

These two materials preparation approaches are illustrated schematically in Figure 1.

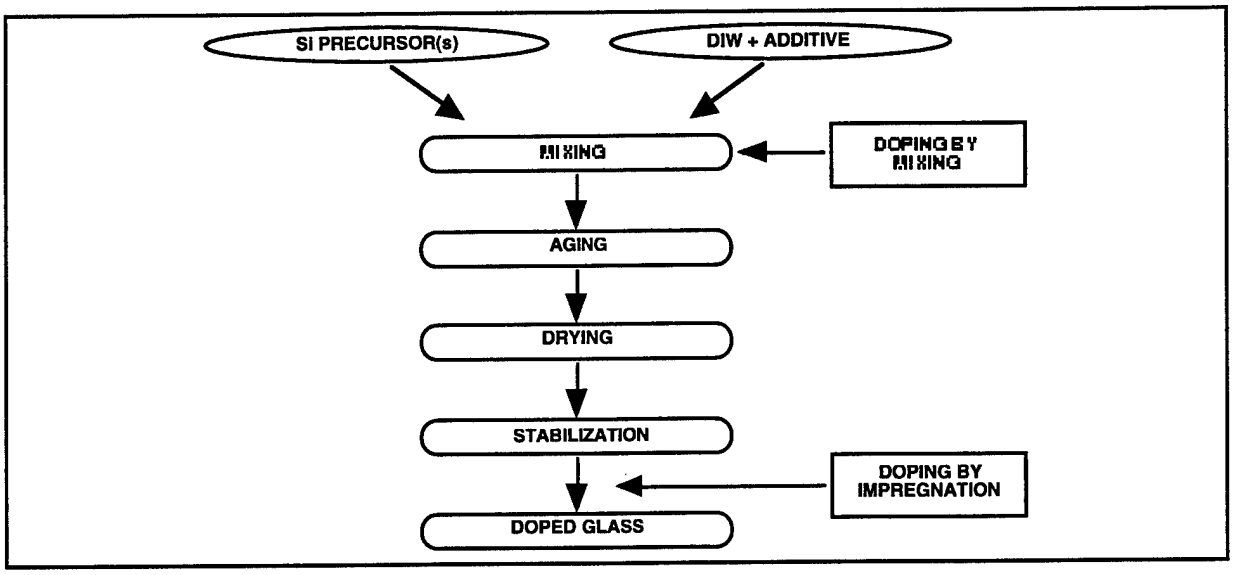

Figure 1: The Sol-Gel Process and the Two Doping Options

In addition to these two synthetic approaches, mold development was also pursued in order to produce doped windows with smooth, flat surfaces with reduced optical scattering losses.

III. PHASE I TECHNICAL OBJECTIVES

The research effort was aimed at two main objectives:

1. Window material preparation, characterization, and optimization
2. Optical quality mold fabrication and development for casting to shape

3.1 Window Material Preparation, Characterization, and Optimization

The preparation of organic glass composites was to be pursued by two approaches:

1. Pre-doping of the glass by adding the optically active organic compound to the sol preparation and subsequently forming the glass at low temperatures, and

2. Post doping porous glass which have been previously fired at high temperatures to maximize their strength and optical quality, then encapsulate the impregnated material.

Characterization methods to be used for glasses prepared by these methods were to include optical power limiting, laser radiation resistance, optical transmission, light scattering, optical homogeneity, surface quality (scratch-dig), and mechanical strength.

3.2 Optical Quality Mold Fabrication and Development for Casting to Shape

Molds for casting the sol-gel glasses were to be designed and fabricated with parallel and optically flat ends. Mold materials were to be investigated which are compatible with the solvents and other chemicals used in the sol-gel compositions. Protective coatings were also to be investigated for compatibility and optical quality. GELTECH is pursuing different mold configurations in developing molding strategies for dense optics applications, and these were to be considered in this development. In this phase the approaches which were to be pursued were to maximize optical quality and give the potential for cost-effective manufacturability in the commercialization phase.

IV. RESULTS OF PHASE I

4.1 Window Material Preparation, Characterization, and Optimization

4.1.1 Characterization of Power Limiting

Power limiting occurs via two mechanisms: transitions between singlet and ground states resulting in picosecond absorption, and transitions between the triplet state and ground state resulting in nanosecond absorption. Figure 2 illustrates these. The total excited-state cross section is the sum of the two. The ratio of the excited-state absorption cross section σ^* to the ground state absorption cross section must be greater than one in order for power limiting to be achieved [1].

Figure 3 represents typical transient absorption, which is directly proportional to the excited-state absorption cross section σ^* [6], of a substituted fullerene over the range of approximately 500 to 800 nm. Measurements are taken on both the femtosecond and nanosecond time scales. Schematics of the measurement systems are given in Figures 4 & 5. The substituted fullerene used extensively for this work is identified as 6,6-phenyl-C61 butylmethoxy (PCBM). Its structure is given in Figure 6.

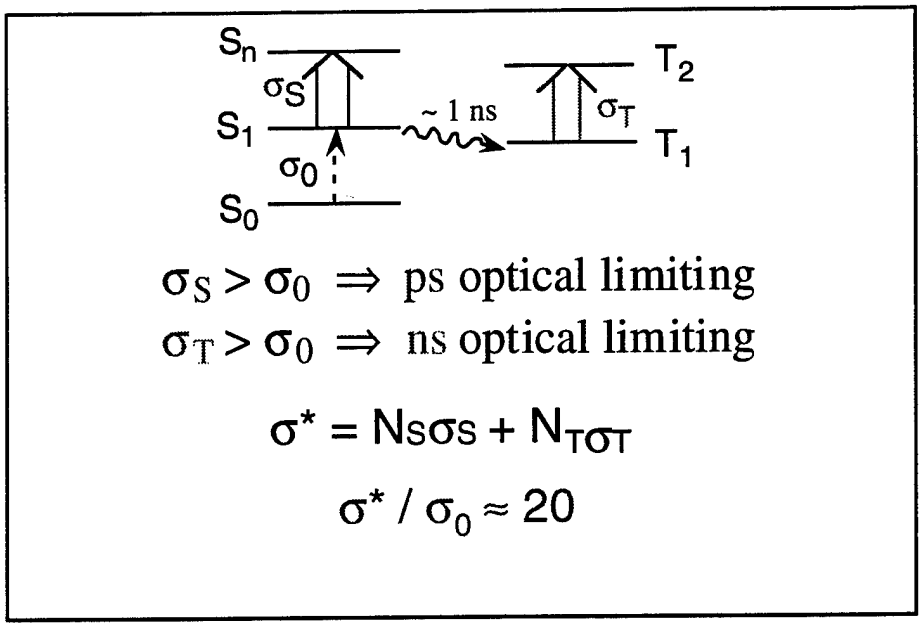

Figure 2: Mechanisms for Optical Limiting

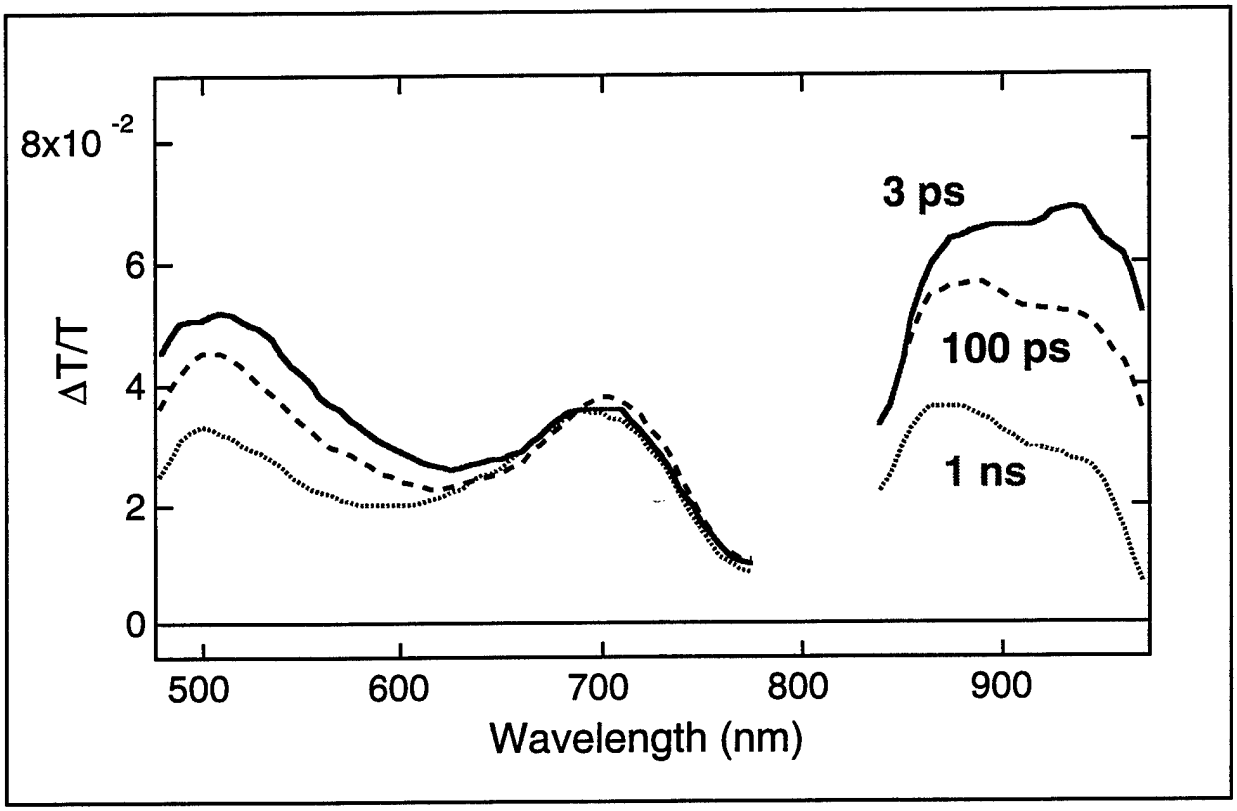

Figure 3: Typical Transient Absorption of Substituted Fullerene

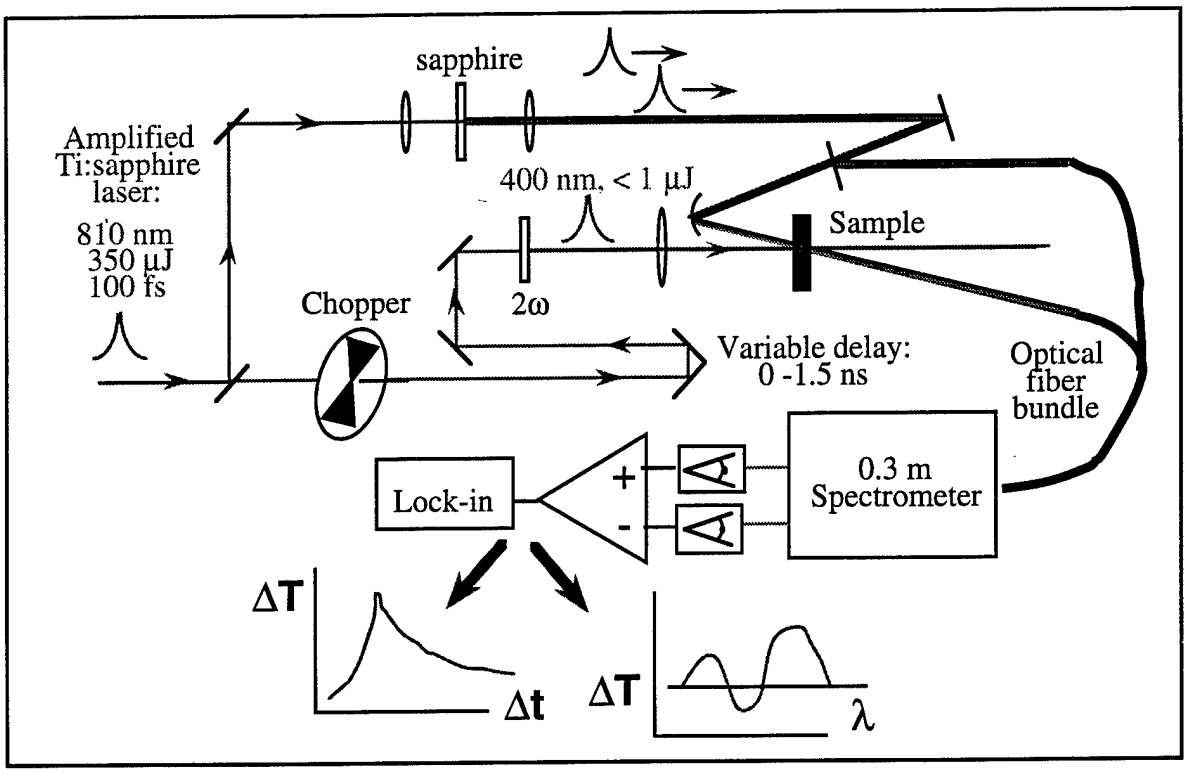

Figure 4: Femtosecond Transient Absorption Spectrometer

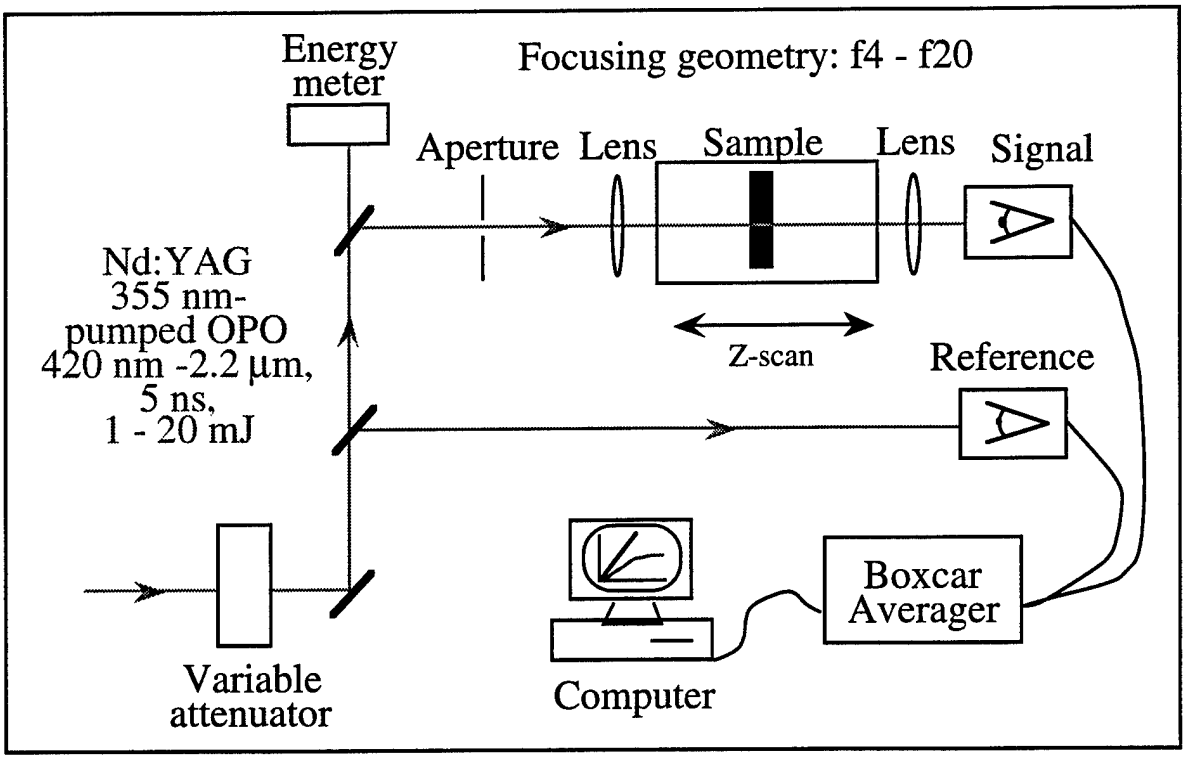

Figure 5: Nanosecond Transient Absorption Spectrometer

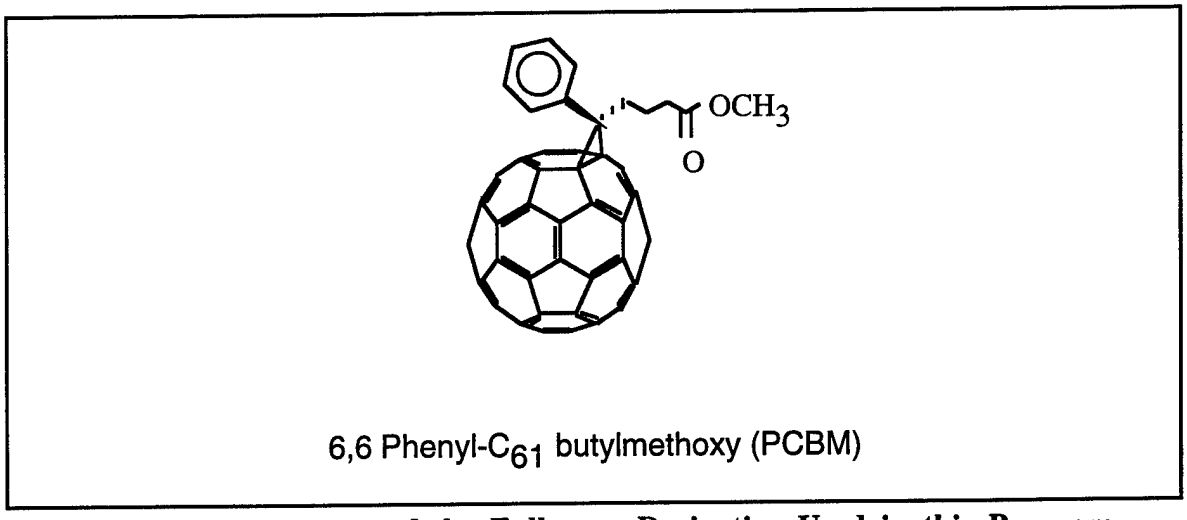

Figure 6: Structure of the Fullerene Derivative Used in this Program

4.1.2 *Results of Materials Preparation by the Pre-doping Approach*

The fullerene compounds being used as active molecules in power limiting are soluble in nonpolar solvents, while the sol-gel compositions required for making the host glasses involve polar conditions. Scientists at Los Alamos National Laboratory have developed patented methods for successfully incorporating these non-polar fullerene compounds into the polar sol-gel glass preparation [10]. The resulting materials show slow (nanosecond) excited-state relaxation dynamics and optical limiting properties similar to those in solution. This ability to control the aggregation of the organic dopant in the glass is essential, since thin solid films of fullerenes show very rapid picosecond relaxation dynamics, and no appreciable optical limiting for ns pulses.

The pre-doped glasses as originally developed had relatively large optical scattering losses (>20%). This scattering was due to a combination of surface roughness, and internal porosity, but the relative contributions had not been determined. Since the improvement of surface roughness was the target of the second main technical objective, the objective of this task was to optimize the pre-doped sol-gel process to reduce porosity, and hence to minimize internal scattering losses, and simultaneously to strengthen the materials. This task investigated two paths: a) reduction of the densification temperature, and b) backfilling of the material pores with a secondary material.

1. Reduction of the Densification Temperature
   The primary obstacle to densification of the organic-doped gels is that silica gels require heat treatment to approximately 1200°C to achieve a fully dense glass. However, no organic guest can survive such extreme temperatures. Fullerenes have proven to be very robust for organic molecules, and can be heated to about 500°C in an oxygen atmosphere before the C60 cage begins to break apart. Hence, one area which was pursued was the addition of B(OH)3 to the glass preparation in order to try to reduce the densification temperature. Several compositions were prepared by varying the B(OH)3 content and the resulting glasses were characterized by BET analysis to determine porosity. Table 1 gives BET data versus densification temperature. The data indicates that densification is taking place between 600° and 700°C. Although this represents a nearly twofold reduction in the densification temperature relative to silica, the temperatures which must be attained for full densification are still prohibitively high for glasses containing organics.

Table 1: BET Data for Fullerene-Doped Glasses Containing 20 wt.% $B(OH)_3$

Densification Temp. (°C)	Specific Surface Area (sq. m./g)	Total Pore Volume (cc/g)
400	282.1	0.171
500	421.2	0.252
600	380.6	0.219
700	6.4	0.006

2. Backfilling of Pores
   An alternative approach to maximizing mechanical and optical properties of the optical limiting windows was also pursued. In this approach the gel pores were filled with a curable silica resin to provide simultaneously both refractive index matching (to reduce scattering losses) and additional mechanical strength. The soluble resin was diffused into the pre-doped porous structures, then these were thermally annealed. Studies were performed to determine the effect of the curable resin on the density, radiation hardness, and power limiting ability of the treated glasses. The effect of successive dopings with the resin was also explored.

   It was found that the maximum amount of resin was incorporated into the glass after two successive backfillings. The treatment was found to enhance the radiation damage threshold of the material by approximately a factor of two, while reducing the porosity as determined from BET measurements by a relatively small amount (approximately 10%). Hence, the improvement of net porosity and associated volume optical scattering losses was slight, however the mechanical strength was significantly improved.

   Despite the relatively minor effect of backfilling on the porosity, significant improvement (greater than 20%) of the net scattering losses was effected on samples with significant surface roughness. Hence, the primary effect of the resin was felt at the surface. Since optical damage occurred most frequently in our tests at the front optical surface, the improvement of surface uniformity and mechanical strength by the resin treatment was likely the most important factor in the enhanced optical damage threshold values for the treated samples. Optical limiting effectiveness was not changed by the backfilling with curable resin.

3. Glasses Pre-doped with Other Dyes
   As an important demonstration of the generality of the synthetic approach developed at LANL for a wide range of organic nonlinear dyes, tailored synthetic procedures have been developed based on pre-doping which allow incorporation of both metallo-porphyrins and metallo-phthalocyanines. The chief difficulty which had to be overcome to achieve this was that the presence of the acid catalyst during the initial sol-gel reaction tends to rapidly destroy the porphyrin, most likely by removal of the central metal atom, resulting in a colorless compound. However, this can be avoided by careful control of the pH of the sol prior to gelation. As shown in Figure 7, the as-prepared wet gel (chemical reactions complete, but still containing toluene co-solvent) has a uv-vis spectrum and color nearly identical to that of the neat compound in solution. Previous efforts resulted in a rapid decoloration of the doped sol in the first few seconds of the gelation reaction. The positions and widths of the absorption bands, as well as the color, are also retained after

heat treatment to 100°C for several hours. The optical limiting performance in the heat-treated gel is lower than that in solution, similar to the results obtained for fullerenes prepared by pre-doping. Determining the microscopic cause of this trend will be the subject of part of the Phase II research.

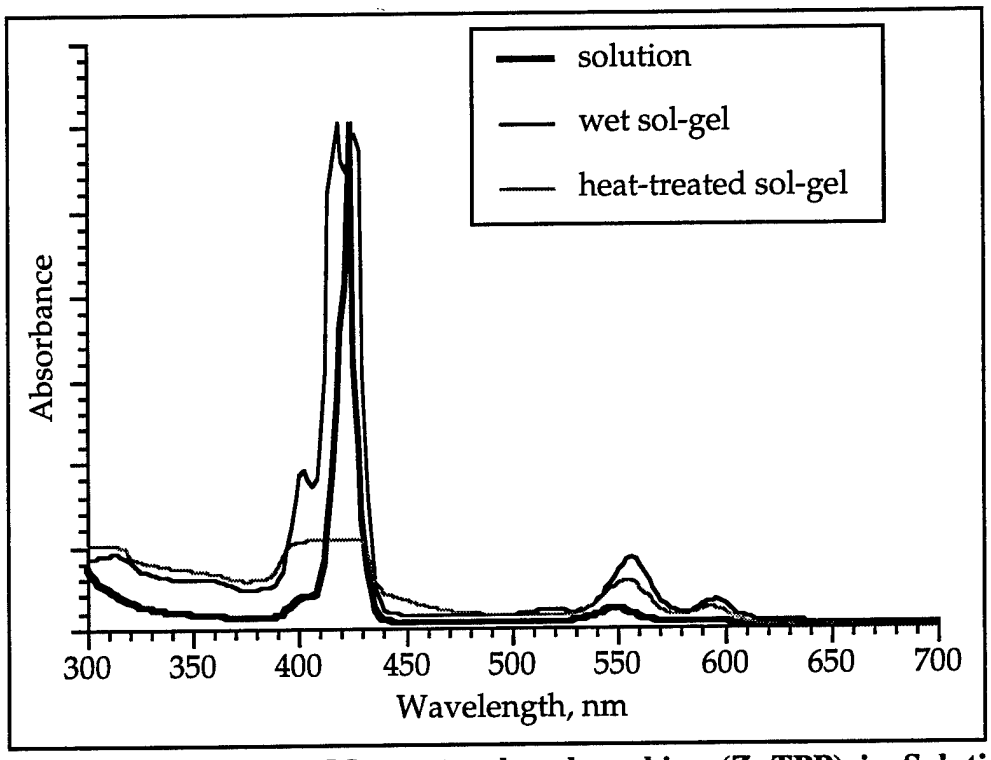

Figure 7: UV-VIS of Zinc Meso-tetraphenylporphine (ZnTPP) in Solution and Sol-Gel Matrix

4.1.3 Results of Materials Preparation by the Post-doping Approach

1. Preparation of Porous Glass Matrices
   A potentially important advantage of the impregnation method is that the matrix can be cured at relatively high temperatures prior to doping. This enhances mechanical strength while retaining porosity. In addition, the pore size and degree of porosity can be tailored to specific applications, creating more design flexibility. At the present time, GELTECH manufactures porous silica in a range of pore sizes: 25, 50, 75, and 200Å nominal pore diameters. For this work the pore diameter glasses used primarily were the 75Å glasses. Smaller pore sizes are more restrictive for the impregnation of the large organic molecules used for power limiting, while the larger pore size glasses have poorer optical quality. Because of their ease of preparation in large quantities, 5.4 mm diameter, 2 mm thick samples were used for the materials preparation in this task.

2. Impregnation of the Porous Matrices
   The mixing method can provide a homogeneous dispersion of the organic molecules in the matrix, and therefore the good isolation or entrapment of the molecules, which is necessary

to their proper optical limiting function. To maintain this effect within the pores of the porous glass, two approaches were pursued:

a) Impregnating the pores with pre-doped sols which were prepared according to the methods of Los Alamos. It was thought that this could provide the best of both approaches, maximizing dispersion of the dopants while making use of the mechanical stability of the porous glass. Backfilling with sol has been reported in the preparation of porous glasses doped with solid state laser dyes [14]. Some porous glasses were prepared in this way. Material preparation was more difficult than other approaches, however, because the glasses had a greater tendency to crack upon filling or redrying. In addition, the power limiting results to date have been poor.

b) Surface treatment of the pore surfaces to reduce their polarity. Because the power limiting compounds are soluble in aromatic solvents, different compounds were used at a range of concentrations for coating the pore surfaces with organic groups. Solutions of the compounds to be used to treat the surfaces were first prepared without the organic dopants, the porous glasses were then impregnated, the solvent was allowed to evaporate from the pores, and the glasses were then heat treated to completely remove solvents and fix the treatment within the pores. Glasses thus prepared were then impregnated with a solution of the power limiting dye, the solvent was again allowed to evaporate from the matrix, and the material was tested for optical performance.

Samples were therefore prepared using the derivatized fullerene compound, PCBM, from Los Alamos National Lab. Initial values of the excited state cross section determined from optical limiting measurements at 650 nm are given in Table 2 for several porous glasses with differing surface treatments. Performance in solution and in the pre-doped sol-gel are given as a reference. Previous work at Los Alamos has shown that the power limiting measured in untreated porous glass is at least an order of magnitude worse than that in solution, and highly variable from spot to spot on the sample. That result is also listed in the table for reference.

Table 2: Power Limiting of Substituted Fullerene vs Host: Excited-State Cross-Section at 650 nm

Compound	Excited State Cross Section (cm2 X 10-18)
PCBM/Toluene	5.5
PCBM/Pre-doped Glass	2.3
PCBM/Untreated Post-dopedGlass	<0.5
PCBM/Post-doped Glass Treatment #1	3.2
PCBM/Post-doped Glass Treatment #2	2.6
PCBM/Post-doped Glass Treatment #3	4.0

As can be seen from the data, the power limiting performance is worst in the untreated, post-doped glasses, and best in toluene solutions. The pre-doped glasses have values of the effective excited-state cross section smaller by more than a factor of two than the solutions. The various proprietary treatments employed in the post-doped glasses all showed significant improvements over the untreated samples, and in the best case the results achieved were nearly as good as those in

solution. Since the solution optical limiting also includes thermal self-defocusing mechanisms which are lower in solid-state samples, it is thought that the solution results represent an upper limit for the performance to be expected in solid samples.

To further determine the optimal treatment concentration for Treatment #3, optical limiting experiments were performed for a series of glasses treated with compound #3 at varying concentration, using otherwise identical conditions. The results of these measurements are listed in Table 3. As described above, the values of the linear transmission for each sample were dependent on position on the sample, with variation of roughly 20% due to the sample nonuniformity. However, despite this variation it was clear that the treatment with the lowest concentration (0.5%) always yielded the best power limiting performance. Treatment with a 1% solution of the active compound gave the most variability (nonuniform limiting performance), while the treatment at the highest concentration yielded more uniform but poorer results.

Table 3: Power Limiting of Post-Doped Glass vs Concentration of Treatment #3:

Compound	Excited State Cross Section (cm2 X 10-18)
PCBM/Post-doped Glass Treatment #3, 0.5%	4.8
PCBM/Post-doped Glass Treatment #3, 1%	3.6
PCBM/Post-doped Glass Treatment #3, 5%	4.0

During the course of the Phase I program contacts were made by both Los Alamos and by GELTECH with Professors David Hagan and Eric Van Stryland at CREOL, the Center for Research and Education in Optics and Lasers at the University of Central Florida. (GELTECH is located next door to CREOL in the Central Florida Research Park.) Profs. Hagan and Van Stryland have been working in the area of power limiting for a number of years, and it was considered to be potentially helpful to the program to have their involvement, initially on an informal basis in Phase I. Their work most recently has been done with Silicon(IV) naphthalocyanines (SiNc), which limit in the visible region.

Porous glass samples were pretreated, as explained above, and doped with the silicon(IV) naphthalocyanine for testing at CREOL. Table 4 gives the results from the most promising of the different samples that were tested.

Table 4: Power Limiting of Silicon(IV) Naphthalocyanine vs Host

Compound	Excited State Cross Section (cm2 X 10-18)
SiNc/Toluene	3.80
SiNc/Untreated Glass	1.62
SiNc/Postdoped Glass Treatment#1	3.09
SiNc/Postdoped Glass Treatment#2	2.35
SiNc/Postdoped Glass Treatment#3	4.1 (at 0.1μJ)
	3.2 (at 0.5 μJ)
SiNc/PMMA (CREOL)	3.52

4.1.4 *Radiation Hardness of Doped Matrices*

Another important issue for the use of power limiting windows in real-life applications is the radiation resistance of the materials. Therefore, damage threshold measurements were made on the different hosts. Damage threshold is listed as the fluence or energy value above which irreversible catastrophic damage is observed in an optical limiting experiment as described above. Table 5 gives the results of these measurements. It was found that the damage correlates best with the total energy deposited on the sample, rather than the fluence, for variation of the f# by a factor of four. The damage threshold in the doped glasses was approximately an order of magnitude larger than that in solution. Some other trends are also observed below:

1. In solution, the damage threshold decreases as the concentration of nonlinear dye increases. The damage mechanism in solution involves both self-focusing effects, and the precipitation of active compound on the front solution cell wall, which lead to damage at the cell/solution interface.

2. The damage threshold of the solid hosts increases as concentration increases, indicating that the nonlinear material protects the sample at the focus, placed for optimal nonlinear effect at the center of the sample.

3. The damage threshold of the pre-doped glasses is affected by the solvent used in their preparation, and the degree of heat treatment to remove all solvent.

4. The damage mechanisms in the post-doped glasses include both a gradual damage or photobleaching, and catastrophic damage due to thermal shock.

Table 5: Damage Threshold vs Host

Compound	Damage Threshold (J/cm2)	Damage Threshold (mJ)
PCBM/Toluene	5 - 20	0.1 ± 0.05
PCBM/Predoped Glass	40 - 200	1.5 ± 0.5
PCBM/Postdoped Glass	40 - 200	1.5 ± 0.5

4.1.5 *Mechanical Testing of Post-Doped glasses*

For a commercial sensor application, GELTECH developed a mechanical test for porous glass matrices. The test is essentially an impact test, whereby a predetermined weight is dropped onto a sampling of porous glass elements and the breakage rate is observed. As a first indication of mechanical suitability of the porous glass for power limiting windows this test was performed on a series of 75Å pore diameter windows. The results indicated that the mechanical strength of these porous glasses was as good or better than the porous glass matrices which have been used commercially. More mechanical testing will be conducted in Phase II, using tests which very closely approximate the final application. If necessary, subsequent treatment or encapsulation of the power limiting glasses can be done to give additional mechanical strength. Treatment of the pre-doped glasses with the curable silica resin as mentioned above has demonstrated an improvement in mechanical strength by such an approach.

4.2 Optical Quality Mold Fabrication and Development for Casting to Shape

The molds for preparing the pre-doped glasses had to fulfill several requirements:

1. The material used had to be compatible with solvents used in the sol-gel formulations. Because the procedure for preparing the glasses requires the use of relatively nonpolar organic solvents, such as toluene or dichlorobenzene, the normal mold materials used by GELTECH for sol-gel preparations were incompatible and a new material had to be found.

2. The surfaces used for molding the faces of the optical windows had to be optical quality, so the material used for this had to be either polishable, or injection moldable to give a high quality optical flat.

3. The material must withstand moderate processing temperatures.

The initial material selected for fabricating optical quality molds was kynar, a polyvinylidene fluoride. The material is very chemically resistant and can be obtained in a grade harder than teflon. Also it can be injection molded. The mold configuration used is shown in Figure 8.

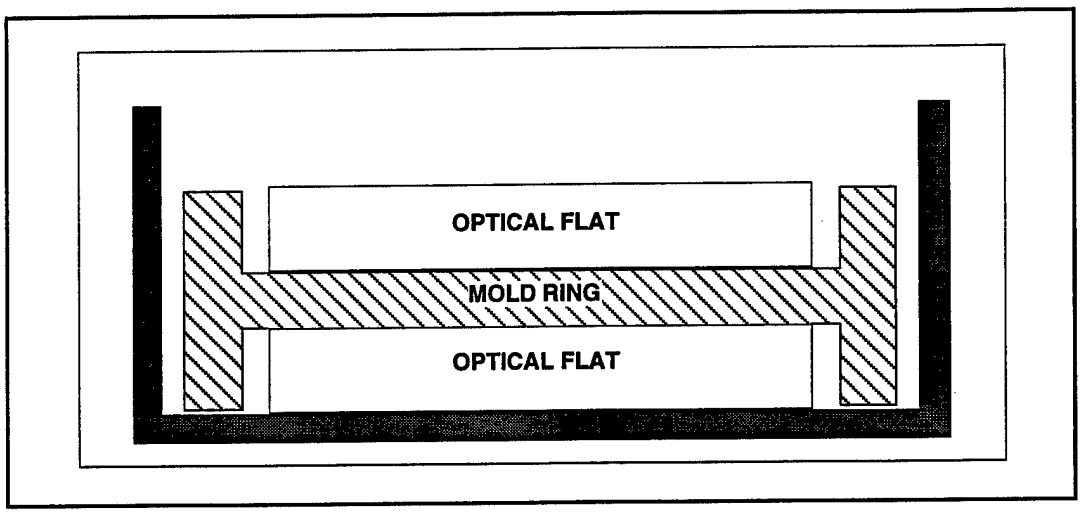

Figure 8: Basic Mold Configuration for Preparation of Pre-doped Windows

Mold rings were machined in-house on a CNC milling machine, and plano discs were optically polished by an outside vendor. Kynar was generally compatible with the solvents used, but was found to give less than optimum surfaces when machined or polished. The molds were used at Los Alamos to produce samples with surfaces that were flat but not good optical quality.

In the pursuit of better materials, a second set of molds was prepared. Mold rings were machined from teflon, which is still fairly soft but machines more cleanly than kynar. The flats used were optically polished silica discs on which a passivating coating had been applied to one face. After coating, the flatness of the parts was measured by interferometry to be better than one half wave deviation, peak-to-valley. Windows prepared with these new molds gave much improved optical surfaces. This improvement was noticeable in two ways. First, the distortion due to lensing by non-planar surfaces was reduced to be acceptable with optical quality to be expected of 2 mm thick

windows. Second, the level of optical scattering relative to non-molded samples was reduced at least four-fold, so that the net scattering loss in the molded glass samples in the visible spectrum was <5%. This indicates that the primary component of optical scattering in the pre-doped glasses previously was surface roughness. This is consistent with BET measurements of the pre-doped gels, which indicated an average pore size of 25 Å. This is too small to contribute significantly to Rayleigh scattering for wavelengths of light in the visible-IR.

One important advantage of this molding approach is that both the materials and the configuration can be adapted to volume production as necessary. GELTECH has already done this for another porous glass product, increasing production capacity to thousands of parts per week.

V. PHASE I SUMMARY AND PLANS FOR PHASE II

The following is a summary of the positive results and remaining problems of the various technical directions which were pursued in Phase I. This will serve as a guide to the technical approach proposed for the Phase II research and development.

The pre-doped sol-gel glasses were developed to the point of being able to manufacture molded optical quality parts with scattering losses reduced to a few % or less. The uniformity of the dopant in these glass samples was excellent, with little variation of linear and nonlinear absorption properties for different spots on a sample, and for different samples in a batch. The two remaining difficulties which must be resolved to develop viable prototype windows using the pre-doping approach are:

The optical limiting performance is reduced in the pre-doped gels relative to that in solution, for both fullerenes and porphyrin samples

The gels are still susceptible to cracking, particularly in moist environments. To address the first problem, we will explore organics from the class of fullerenes and porphyrins derivatized so that the substituent groups act to mediate the interface between the organic dye and the inorganic host in a similar manner as that found to be effective in improving the performance of the post-doped glasses. To address the second problem, we will investigate organically-modified silica gels (ORMOSILs) which contain a small amount of structural polymer designed to enhance the mechanical strength of the host matrix.

The post-doped glasses were developed to the point that we demonstrated a control of the optical limiting performance based on different pretreatment regimes prior to introducing the nonlinear organic guest. It was found that with optimal treatment, the power limiting characteristics were equivalent to those in solution, while the advantages of using a silica host were preserved (moldable shape and high optical damage threshold). The primary remaining difficulty in using this approach is that the resulting glasses were nonuniform, with variations of the linear and nonlinear transmittance by as much as 20%. The origin of this nonuniformity, and the means of controlling it by varying the pore structure of the porous gel host, will be the primary goal of Phase II research on this topic.

Additionally, a vital component of the Phase II development work will be to adapt the synthetic procedures developed in Phase I for optimal use with the nonlinear dyes considered by R&D experts from the various service branches to be the most promising for near-term applications in the field. To facilitate this development, we have initiated substantive contacts with three R&D

Centers with close ties to this area. They are the following: U.S. Army Natick R&D Center, U.S. Army Tank and Automotive R,D&E Center, and U.S. Naval Research Laboratory. We have commitments from people at each of these centers to continue close interactions within the scope of our Phase II work, if funded, especially with respect to new organic absorber development, and device designs incorporating our prototype windows for field-testable imaging systems.

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